

Technical I

Technical Field

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Abstract

Furthermore, it has been known for a long time to form a protective film in contact with a recording film to inhibit deformation of the recording film, and it has been proposed to contain nitrogen in the protective film to make the protective film denser and enhance the mechanical strength (JP-B-7-111786).

With a recent wide spread of the above-mentioned information recording media which carry out recording, erasing and reproduction of information by irradiation with laser beams, namely, so-called optical disks, these are often used and stored in a severer environment. Thus, it is needed to improve reliability of optical disks more than before. From such a viewpoint, various environmental resistance tests have been conducted, and as a result, there has been found a problem that when a disk in which an information has been once recorded is stored for a long time in a severe environment of high temperature and high humidity and then overwriting is carried out in the same portion as recorded, a writing error is caused. This is examined in detail to find that the once recorded amorphous mark is not erased by the overwriting and remains. It is considered that this is because some changes in properties occur in the amorphous mark due to the leaving in a severe environment. Details of the changes in properties are not clear, but they seem to include oxidation of the amorphous mark and aggregation of impurities present in the recording film. Thus, it is considered that the changes in properties hinder the

formation of crystal nuclei which play an important roll in the crystallization process (erasing process) of the amorphous mark, thereby causing failure in overwriting. In any way, that the once written information cannot be
5 rewritten means that information in file management area or defect management area can also be not rewritten, and this may cause serious troubles in the market.

Accordingly, the object of the present invention is to solve the above problems and provide an information
10 recording medium superior in reliability even in a severe environment.

Disclosure of Invention

As a result of intensive research conducted by
15 the inventors in an attempt to attain the object, it has been found that in an information recording medium having a construction comprising a recording film and a protective film formed in contact with the recording film, the state of the interface between the recording film and
20 the protective film is very important, and the above problems can be solved by taking into consideration the content of nitrogen around the interface.

That is, it has been found that in an information recording medium comprising a substrate on
25 which at least a recording film which undergoes change in atomic arrangement upon irradiation with recording beams and a protective film comprising a dielectric are formed in contact with each other, when contents of nitrogen on

both sides of the interface at which the recording film and the protective film contact with each other are allowed to differ from each other and when the changing amount of the nitrogen content in the direction of thickness of the film with the interface between the films as a boundary is 1-50 at.%/nm, the above problems can be completely solved.

As one embodiment, the nitrogen content on the recording film side is larger than that on the protective film side with the interface between the films as a boundary, and the nitrogen content in the recording film near the interface is larger than the nitrogen content in the inner part of the recording film. In this case, the recording film may comprise a layer of larger nitrogen content and a layer of smaller nitrogen content. Alternatively, the nitrogen content in the recording film may be such that it continuously decreases from the interface towards the inner part.

As another embodiment, the nitrogen content on the protective film side is larger than that on the recording film side with the interface between the films as a boundary, and the protective film contains as a main component a nitride of at least one of the elements constituting the recording film.

As further embodiment, the nitrogen content on the protective film side is larger than that on the recording film side with the interface between the films as a boundary, and the protective film contains a sulfide

as one of main components. In this case, the recording film preferably contains at least one element selected from Si, P, V, Mn, Fe, Co, Ni, Cu, Zn, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Sn, Ta, Os, Ir, Pt, Au, Tl, Pb, Bi and Cr. It is
5 further preferred that the sulfide is zinc sulfide and the nitrogen content in the protective film is not more than 25 at.%. Content of at least one element selected from Si, P, V, Mn, Fe, Co, Ni, Cu, Zn, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Sn, Ta, Os, Ir, Pt, Au, Tl, Pb, Bi and Cr contained in the
10 recording film is preferably 0.1-10 at.%.

Hitherto, it has been considered that formation of crystal nuclei more readily occurs in the area where composition abruptly or discontinuously changes, such as an interface between a recording film and a protective
15 film, namely, so-called peculiar point, and an experimental fact has been known which supports the hypothesis that in a normal environment, the crystal nuclei are formed at the interface and crystal grows around the nuclei. However, as mentioned above, after left
20 in a severe environment, the interface changes in properties, and there may occur a phenomenon that even if there is a discontinuity of the composition, the crystal nuclei are formed with difficulty and the crystallization does not proceed. On the other hand, it can be presumed
25 that when the nitrogen content has a gradient of more than a certain level with the interface between the films as a boundary and the nitrogen content is abruptly changed as in the present invention, the changing point behaves as a

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Brief Description of Drawings

FIG. 1 is a sectional view of the information recording medium obtained in Experimental Example 1 of the

present invention. FIG. 2 is a sectional view of the information recording medium obtained in Experimental Example 2 of the present invention. FIG. 3 is a sectional view of the information recording medium obtained in
5 Experimental Example 3 of the present invention.

Best Mode for Carrying Out the Invention

There are considered various methods for changing the nitrogen content with the interface between
10 the films as a boundary. The method of increasing the nitrogen content in the recording film than that in the protective film has the merit that the nitrogen content in the recording film can be relatively freely selected and the gradient of the nitrogen content with the interface
15 between the films as a boundary can be readily controlled. However, at the same time, there is caused a disadvantage that the melting point increases and the recording sensitivity lowers, and, thus, preferred is a method of containing nitrogen in only the recording film in the
20 vicinity of the interface between the recording film and the protective film. This method can easily control the gradient of the nitrogen content without causing deterioration of the recording sensitivity, and there are a method of forming a layer of large nitrogen content at
25 only the interface with the protective film and a method of continuously reducing the nitrogen content from the interface between the recording film and the protective film towards the inner part of the recording film. In the

former method, thickness of the layer of large nitrogen content is preferably 1-5 nm. However, these methods have the defects that since the recording film comprises a multilayer, the film constitution becomes complicated and
5 since the nitrogen content is continuously changed, the process becomes complicated.

In the case of increasing the nitrogen content in the protective film than that in the recording film, when at least one of the main components of the material
10 forming the protective film is a nitride of the element constituting the recording film, the recording film and the protective film contain the same element, and thus there is the merit that the formation of crystal nuclei at the interface is readily accelerated. However, there is a
15 defect that owing to an optical need that the protective film containing a nitride as a main component must be transparent to the laser wavelength for recording and reproduction, the nitrogen content is restricted to some extent and, hence, the gradient of the nitrogen content
20 with the interface between the films as a boundary cannot be freely selected. Furthermore, the nitride is high in heat conductivity to cause a trouble of deterioration in recording sensitivity. In the case of using a nitride as the protective film, a construction which is optically
25 transparent and less in restriction of the nitrogen content can be formed by continuously or discontinuously changing the nitrogen content in the vicinity of the interface and the content in the area apart from the

interface. Moreover, when a sulfide which is lower in heat conductivity than nitride is used as the material of the protective film, there is a merit that decrease of recording sensitivity is not brought about with ease. The sulfide is preferably zinc sulfide, and a mixture of zinc sulfide and silicon dioxide is lower in heat conductivity and is more preferred. However, when a material mainly composed of a sulfide is used as the protective film, there occur a phenomena that sulfur diffuses into the recording film by carrying out rewriting many times to cause increase of jitter. This phenomenon occurs more conspicuously in case nitrogen is contained in a large amount in the sulfide protective film. The reason for this deterioration is that optical constants of the recording film and crystallization rate change from the initial state due to the diffusion of sulfur. In this case, therefore, when elements which hardly cause diffusion of sulfur or do not deteriorate the optical constants or crystallization rate even if the diffusion occurs, namely, at least one element of Si, P, V, Mn, Fe, Co, Ni, Cu, Zn, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Sn, Ta, Os, Ir, Pt, Au, Tl, Pb, Bi and Cr, are contained in the recording film, the number of times of rewriting increases and this is preferred. These elements bond to the diffused sulfur to produce sulfides or to produce a barrier layer inhibiting the diffusion of sulfur, and thus have the effect to inhibit an adverse influence caused by the diffusion of sulfur. Of these elements, preferred are Co, Pd, Ag, Ta, Pt, Au, Tl

As the recording films, there may be used as main components the known materials such as Ge-Sb-Te based materials, In-Sb-Te based materials, Ag-In-Sb-Te based materials and In-Se based materials.

The present invention will be explained in detail by the following examples.

A substrate 1 was prepared which comprised a polycarbonate resin sheet of 120 mm in diameter and 0.6 mm in thickness on the surface of which were previously formed embossed pits containing address information and the like and U-shaped grooves of 0.74 μm in width and 65 nm in depth at a pitch of 1.48 μm . This substrate 1 was placed in the first sputtering chamber in a sputtering apparatus having a plurality of sputtering chambers and

excellent in formation of uniformity of film thickness and reproducibility. A $(\text{ZnS})_{80}(\text{SiO}_2)_{20}$ (mol%) first protective layer 2 having a thickness of 90 nm was formed using a mixture of ZnS and SiO_2 as a target in an argon gas. Then, this substrate was transferred to the second sputtering chamber, and a chromium oxide interface film 3 having a thickness of 10 nm was formed in an argon gas using chromium oxide as a target. This interface film 3 had an effect to inhibit diffusion of S or the like in the first protective film comprising ZnS- SiO_2 . Furthermore, this substrate was transferred to the third sputtering chamber, and first an Ag-Ge-Sb-Te-N film (nitride recording film) 4 of 1 nm was formed using $\text{Ag}_{2.5}\text{Ge}_{20}\text{Sb}_{22.5}\text{Te}_{55}$ (at.%) sintered body as a target in a mixed gas of argon and nitrogen, and then an $\text{Ag}_{2.5}\text{Ge}_{20}\text{Sb}_{22.5}\text{Te}_{55}$ (at.%) recording film 5 of 14 nm was formed with changing the gas to argon gas. The nitrogen content in the mixed gas used for the formation of the nitride recording film was 20 mol%. Then, the substrate was transferred to the fourth sputtering chamber and a $(\text{ZnS})_{80}(\text{SiO}_2)_{20}$ (mol%) second protective layer 6 having a thickness of 15 nm was formed in the same manner as in the formation of the first protective layer. Then, an $\text{Al}_{94}\text{Cr}_6$ (at.%) first reflective layer 7 having a thickness of 68 nm was formed using an AlCr alloy as a target in the fifth chamber. Finally, an $\text{Al}_{99}\text{Ti}_1$ (wt.%) second reflective layer 8 of 22 nm was formed using an AlTi alloy as a target in the sixth chamber. The laminate substrate was taken out from the sputtering apparatus, and

an ultraviolet curing resin protective layer 9 was formed by spin coating on the uppermost layer.

In the same manner as above, on another same substrate 1' were formed a $(\text{ZnS})_{80}(\text{SiO}_2)_{20}$ (mol%) first protective layer 2', a chromium oxide interface film 3', an Ag-Ge-Sb-Te-N film (nitride recording film) 4', an $\text{Ag}_{2.5}\text{Ge}_{20}\text{Sb}_{22.5}\text{Te}_{55}$ (at.%) recording film 5', a $(\text{ZnS})_{80}(\text{SiO}_2)_{20}$ (mol%) second protective layer 6', an $\text{Al}_{94}\text{Cr}_6$ (at.%) first reflective layer 7', an $\text{Al}_{99}\text{Ti}_1$ (wt.%) second reflective layer 8', and an ultraviolet curing resin protective layer 9'. The resulting two substrates were laminated with an adhesive layer 10 so that the ultraviolet curing resin layers 9 and 9' faced each other with the adhesive layer 10 therebetween. In this case, when the diameter of the adhesive layer was not less than 118 mm, the adhesive layer was hardly peeled by a shock such as falling.

The thus obtained disk was referred to as A1. In the case of the disk A1, the change of the nitrogen content with the interface between the nitride recording film and the protective film as a boundary can be changed by changing the nitrogen content in the argon-nitrogen mixed gas in the formation of the Ag-Ge-Sb-Te-N film (nitride recording film) 4.

Experimental Example 2

The same substrate 1 as of Experimental Example 1 was placed in the first sputtering chamber in a sputtering apparatus having a plurality of sputtering

chambers and excellent in formation of uniformity of film thickness and reproducibility. A $(\text{ZnS})_{80}(\text{SiO}_2)_{20}$ (mol%) first protective layer 2 having a thickness of 90 nm was formed in an argon gas using a mixture of ZnS and SiO_2 as a target. Then, this substrate was transferred to the second sputtering chamber, and a chromium oxide interface film 3 having a thickness of 20 nm was formed in an argon gas using chromium oxide as a target. This interface film 3 had an effect to inhibit diffusion of S or the like in the first protective film comprising ZnS- SiO_2 . Furthermore, this substrate was transferred to the third sputtering chamber, and an $\text{Ag}_{2.5}\text{Ge}_{20}\text{Sb}_{22.5}\text{Te}_{55}$ (at.%) recording film 5 of 16 nm was formed in an argon gas using an $\text{Ag}_{2.5}\text{Ge}_{20}\text{Sb}_{22.5}\text{Te}_{55}$ (at.%) sintered body as a target. Then, the substrate was transferred to the fourth sputtering chamber and a Ta-N second protective layer 11 having a thickness of 18 nm was formed in a mixed gas of argon and nitrogen using a Ta-N sintered body as a target. The nitrogen content in the mixed gas was 40 mol%. Then, an $\text{Al}_{94}\text{Cr}_6$ (at.%) first reflective layer 7 of 35 nm was formed using an AlCr alloy as a target in the fifth chamber. Finally, an $\text{Al}_{99}\text{Ti}_1$ (wt.%) second reflective layer 8 of 35 nm was formed using an AlTi alloy as a target in the sixth chamber. The laminate substrate was taken out from the sputtering apparatus, and an ultraviolet curing resin protective layer 9 was formed by spin coating on the uppermost layer.

In the same manner as above, on another same substrate 1' were formed a $(\text{ZnS})_{80}(\text{SiO}_2)_{20}$ (mol%) first

protective layer 2', a chromium oxide interface film 3',
 an $\text{Ag}_{2.5}\text{Ge}_{20}\text{Sb}_{22.5}\text{Te}_{55}$ (at.%) recording film 5', a Ta-N second
 protective layer 11', an $\text{Al}_{94}\text{Cr}_6$ (at.%) first reflective
 layer 7', an $\text{Al}_{99}\text{Ti}_1$ (wt.%) second reflective layer 8', and
 5 an ultraviolet curing resin protective layer 9'. The
 resulting two substrates were laminated with an adhesive
 layer 10 so that the ultraviolet curing resin layers 9 and
 9' faced each other with the adhesive layer 10
 therebetween. In this case, when the diameter of the
 10 adhesive layer was not less than 118 mm, the adhesive
 layer was hardly peeled by a shock such as falling.

The thus obtained disk was referred to as A2. In
 the case of the disk A2, the change of the nitrogen
 content with the interface between the nitride recording
 15 film and the protective film as a boundary can be changed
 by changing the nitride content in the argon-nitrogen
 mixed gas in the formation of the Ta-N second protective
 layer 11.

20 Experimental Example 3

The same substrate 1 as of Experimental Example
 1 was placed in the first sputtering chamber in a
 sputtering apparatus having a plurality of sputtering
 chambers and excellent in formation of uniformity of film
 25 thickness and reproducibility. A $(\text{ZnS})_{80}(\text{SiO}_2)_{20}$ (mol%)
 first protective layer 2 having a thickness of 90 nm was
 formed in an argon gas using a mixture of ZnS and SiO_2 as a
 target. Then, this substrate was transferred to the second

sputtering chamber, and a chromium oxide interface film 3 having a thickness of 20 nm was formed in an argon gas using chromium oxide as a target. This interface film 3 had an effect to inhibit diffusion of S or the like in the first protective film comprising ZnS-SiO₂. Furthermore, this substrate was transferred to the third sputtering chamber, and an Ag_{2.5}Ge₂₀Sb_{22.5}Te₅₅ (at.%) recording film 5 of 16 nm was formed in an argon gas using an Ag_{2.5}Ge₂₀Sb_{22.5}Te₅₅ (at.%) sintered body as a target. Then, the substrate was transferred to the fourth sputtering chamber and a ZnS-SiO₂-N second protective layer 12 having a thickness of 18 nm was formed in a mixed gas of argon and nitrogen using a mixture of ZnS and SiO₂ as a target. The nitrogen content in the mixed gas was 2 mol%. Then, an Al₉₄Cr₆ (at.%) first reflective layer 7 of 35 nm was formed using an AlCr alloy as a target in the fifth chamber. Finally, an Al₉₉Ti₁ (wt.%) second reflective layer 8 of 35 nm was formed using an AlTi alloy as a target in the sixth chamber. The laminate substrate was taken out from the sputtering apparatus, and an ultraviolet curing resin protective layer 9 was formed by spin coating on the uppermost layer.

In the same manner as above, on another same substrate 1' were formed a (ZnS)₈₀(SiO₂)₂₀ (mol%) first protective layer 2', a chromium oxide interface film 3', an Ag_{2.5}Ge₂₀Sb_{22.5}Te₅₅ (at.%) recording film 5', a ZnS-SiO₂-N second protective layer 12', an Al₉₄Cr₆ (at.%) first reflective layer 7', an Al₉₉Ti₁ (wt.%) second reflective layer 8', and an ultraviolet curing resin protective layer

9'. The resulting two substrates were laminated with an adhesive layer 10 so that the ultraviolet curing resin layers 9 and 9' faced each other with the adhesive layer 10 therebetween. In this case, when the diameter of the adhesive layer was not less than 118 mm, the adhesive layer was hardly peeled by a shock such as falling.

The thus obtained disk was referred to as A3. In the case of the disk A3, the change of the nitrogen content with the interface between the nitride recording film and the protective film being a boundary can be changed by changing the nitrogen content in the argon-nitrogen mixed gas used in the formation of the ZnS-SiO₂-N second protective layer 11.

15 Comparative Example

A disk was prepared in the same manner as in the Experimental Example 1, except that in place of the ZnS-SiO₂-N film, a (ZnS)₈₀(SiO₂)₂₀ film was formed in the fourth sputtering chamber. This disk was referred to as B1.

Each of the resulting disks A1, A2, A3 and B1 was rotated at a linear speed of 6 m/s, and the recording film was irradiated through the substrate with semiconductor laser beams of 660 nm in wavelength condensed by an objective lens of NA 0.6 to perform recording and reproduction. For recording, a waveform obtained by modulating the laser power between 11 mW and 5 mW, and a random signal modulated by 8-16 was recorded. A direct overwriting was conducted by forming a record mark

with a power of 11 mW and erasing it with a power of 5 mW. However, a multi pulse recording waveform which divides record pulse into a plurality of pulses was used other than for the shortest mark.

5 When a random signal was recorded in the above disks, jitter was not more than 8.5% in all disks. On the other hand, when data were recorded in these disks, these disks were left to stand for 500 hours in an environment of 80°C and 90%RH, then the same place as recorded was
10 subjected to direct overwriting with a random signal, and jitter was measured, a jitter of not more than 8.5% which was the same as before introduction into the environment in the disks A1, A2 and A3, but jitter was not less than 15% in the disk B1 and thus deterioration was seen in
15 overwriting characteristics.

 Gradient of nitrogen content at the interface between the recording film and the protective film in each of the disks A1, A2, A3 and B1 was measured by Auger electron spectroscopy to obtain 3 at.%/nm in the disk A1,
20 30 at.%/nm in the disk A2, 7 at.%/nm in the disk A3, and 0 at.%/nm in the disk B1.

 Conditions for forming films containing nitrogen in each of the disks A1, A2 and A3 were investigated, and each thirty disks for each of several kinds of disks
25 differing in change of the nitrogen content with the interface between the recording film and the protective film as a boundary were prepared. A random signal was recorded in all of these disks, and these disks were left

to stand for 500 hours in an environment of 80°C and 90%RH, then the same place as recorded was subjected to direct overwriting with random signal, and jitter was measured. In the case of the gradient of the nitrogen content being 0.5 at.%/nm, the jitter after overwriting exceeded 15% in not less than 10 disks of the disks A1, A2 and A3, respectively. However, in the case of 1 at.%/nm, 50 at.%/nm or 60 at.%/nm, the jitter after overwriting exceeded 15% in none of the disks. On the other hand, a random signal was recorded in all of the disks, and these disks were left to stand for 500 hours in an environment of 80°C and 90%RH, then recorded data were reproduced and jitter was measured. In the case of 0.5 at.%/nm, 1 at.%/nm or 50 at.%/nm, the jitter exceeded 15% in none of the disks, while in the case of 60 at.%/nm, the jitter exceeded 15% in not less than 10 disks of the respective disks. In the above experiments, the disks A2 in which the gradient of the nitrogen content at the interface was 0.5 at.%/nm and 1 at.%/nm had such construction that the nitrogen content in the vicinity of the interface with the recording film was smaller than the nitrogen content in the inner part of the protective film.

The similar results were obtained in the disk A1 when, in the production of the disk, the nitrogen content in the recording film was continuously changed by continuously changing the nitrogen content in the gas at the time of changing the sputtering gas from the mixed gas of argon and nitrogen to argon in the third sputtering

chamber.

Furthermore, the similar results were obtained when a part or the whole of Ag contained in the recording film is replaced with Si, P, V, Mn, Fe, Co, Ni, Cu, Zn, Nb, Mo, Ru, Rh, Pd, Cd, Sn, Ta, Os, Ir, Pt, Au, Tl, Pb, Bi and Cr. Among them, preferred are Co, Pd, Ta, Pt, Au, Tl and Cr. When amount of these elements was less than 0.1 at.%, the number of times of rewriting decreased. The effect of addition of these elements was most conspicuous in A3. However, when the amount exceeded 10 at.%, the initial jitter became somewhat inferior.

The number of times of rewriting also decreased when the nitrogen content in the ZnS-SiO₂-N film in A3 exceeded 25 at.%.

Industrial Applicability

As explained above, according to the present invention, information recording media excellent in reliability of information even if left in a severe environment could be obtained.